Fourth Annual Conference on Carbon Capture & Sequestration

Developing Potential Paths Forward Based on the Knowledge, Science and Experience to Date

Advanced Conversion/Capture Concepts

Carbon Sequestration in Waste Mineral Byproducts

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Research Objectives for this Preliminary Study

- Determine whether it is feasible to sequester CO_2 using calcium oxide minerals and cement kiln dust

- Measure the extent and rate of sequestration

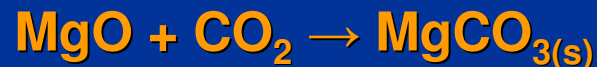- Examine the influence of water on the extent and rate of sequestration

Mineral Carbonation

- Alkaline metal oxides (MgO and CaO) react with CO_2 to produce calcite ($CaCO_3$) and magnesite ($MgCO_3$)

  Carbonate is lowest energy-state of carbon; and carbonation reactions are highly exothermic:

  $$CaO + CO_2 \rightarrow CaCO_{3(s)}$$

  $(\Delta H = -179 \text{ kJ/mol})$

  $$MgO + CO_2 \rightarrow MgCO_{3(s)}$$
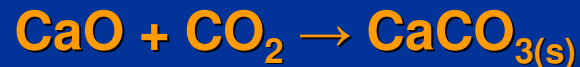
  $(\Delta H = -118 \text{ kJ/mol})$

- Naturally occurring rock weathering process is very slow

Enhancing Mineral Carbonation

- Adding heat

- Increasing Pressure (P_{CO2})

- Extracting/concentrating oxides

- Increasing surface area
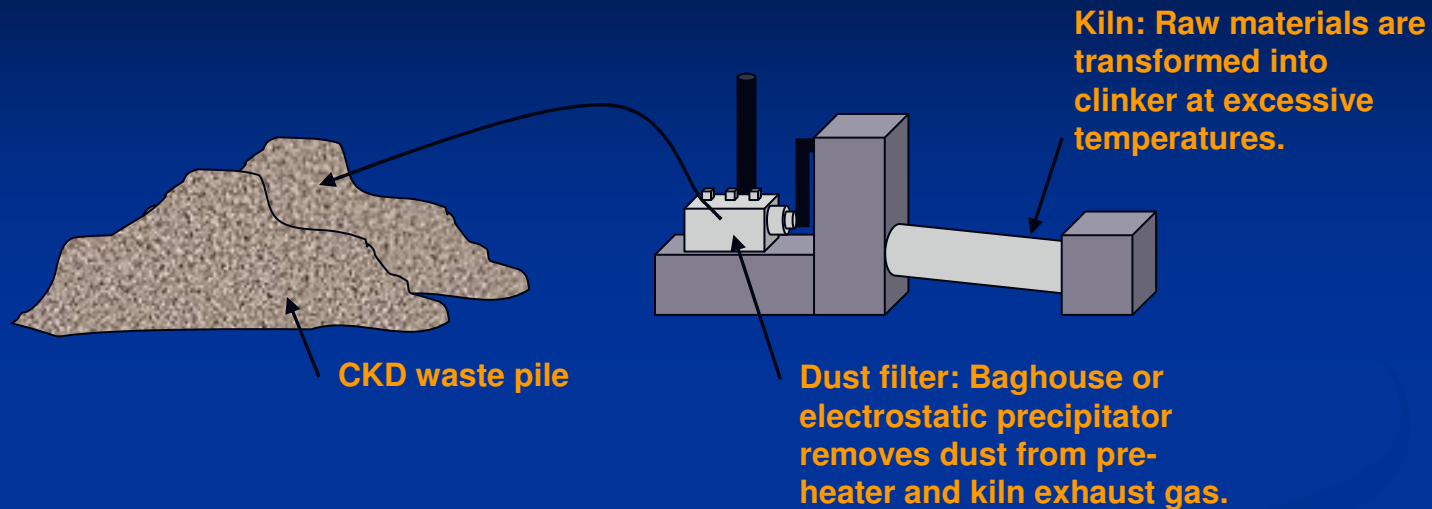
Alkaline Waste Byproducts

- Cement kiln dust, coal fly ash, etc.

- High surface area

- Little or no need for processing

- Typically high in calcium and/or magnesium oxides

- Generally available in large quantities

- Reaction with CO_2 neutralizes waste

Cement Manufacturing

- Third largest source of process-related CO_2 emissions

- U.S. cement industry alone produces > 90 Tg CO_2 annually (>800 Tg CO_2 globally)

- ~5% of the global CO_2 emissions

- CO_2 originates both from the calcining process and the burning of fossil fuels

- U.S. is 3rd largest cement producer

- Millions of tons of waste/byproducts produced annually

*Sources: Hanle et al 2004; EPA 2004, 1999; PCA 2003; van Oss and Padovani 2003

Cement Kiln Dust (CKD)

Kiln: Raw materials are transformed into clinker at excessive temperatures.

CKD waste pile

Dust filter: Baghouse or electrostatic precipitator removes dust from pre-heater and kiln exhaust gas.

- 20 – 60% CaO

- High surface area (>800 m²/kg; PCA 2003)

- 8 to 12 million tons produced annually in U.S. alone (EPA 1999; PCA 2003; van Oss and Padovani 2003)

- A majority of CKD is disposed of or stockpiled on site, only a fraction is recycled into the process line
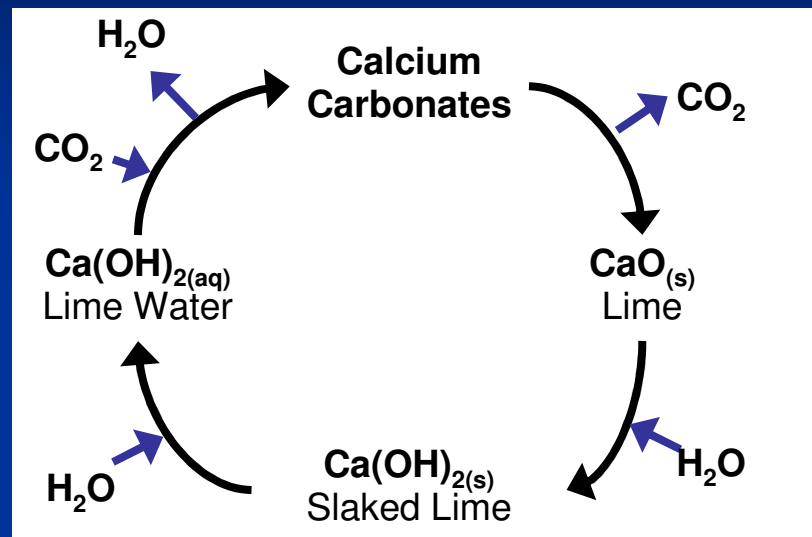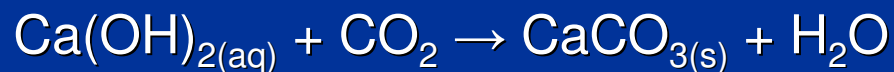
Carbonation Reactions using CKD

High surface area and open pore structure reduces need for processing, increases reaction rate, and decreases the overall energy requirements of the process.

Sequestration by CaO:

$$CO_{2(g)} \leftrightarrow CO_{2(aq)}$$

$$(K_H = 10^{-1.5} \text{ moles/L·atm})$$

$$CaO_{(s)} + H_2O \rightarrow Ca(OH)_{2(s)}$$

$$Ca(OH)_{2(s)} \leftrightarrow Ca(OH)_{2(aq)}$$

$$Ca(OH)_{2(aq)} + CO_2 \rightarrow CaCO_{3(s)} + H_2O$$

Overall Reaction:

$$CaO_{(s)} + CO_{2(aq)} \rightarrow CaCO_{3(s)}$$

Significance of CO$_2$ Sequestration

- *Landfilled* CKD has the potential to capture 10% of the process-related emissions from the U.S. cement industry alone

- Carbonation process neutralizes wastes high in CaO and MgO; reducing leaching capacity

- End-products can be used for beneficial purposes such as road base, etc.

Preliminary Experiments

■ Batch Experiments

- CaO, $Ca(OH)_2$, and CKD

- Tedlar Bags

- Pure grade CO_2 and N_2 (matrix gas)

- Initial CO_2 concentrations ranging from 50,000 to 100,000 ppm_v

- Additional moisture added

- Duration: several hours to 1.4 days

■ Column Experiments

- CKD and $Ca(OH)_2$

- Core and glass columns

- Pure grade CO_2 and N_2 (matrix gas)

- Influent CO_2 concentration ranging from 50,000 to 100,000 ppm_v

- No moisture additional added

- Duration: 1 to 14 days.

Preliminary Batch Experiments

Concentration of CO_2 with time during batch experiment with Cement Kiln Dust (CKD), before adding water

$\ln[CO_2] = -0.75t - 5.5$
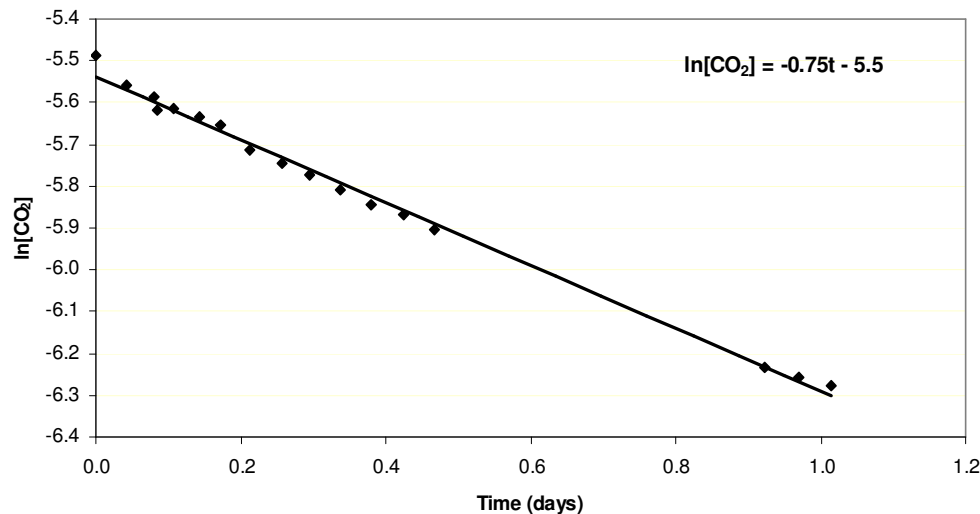
Concentration of CO_2 with time during batch experiment with Cement Kiln Dust (CKD), after adding water
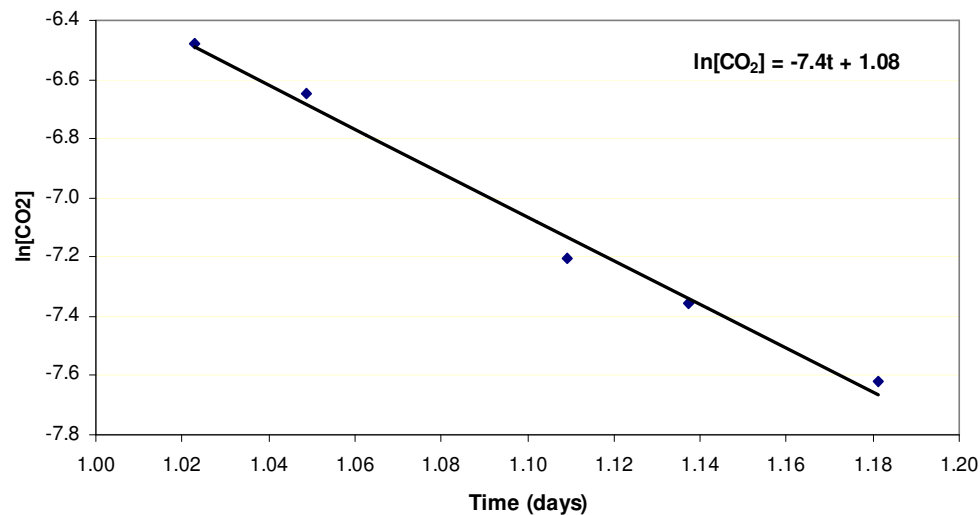

$\ln[CO_2] = -7.4t + 1.08$

Initial Mass of CKD = 0.627 g

Initial CO_2 = 103,366 ppm$_v$

- Pseudo-first order reaction kinetics (at early times)

- Rate constant increased by an order of magnitude upon addition of water

Preliminary Column Experiments
CKD Core Segment
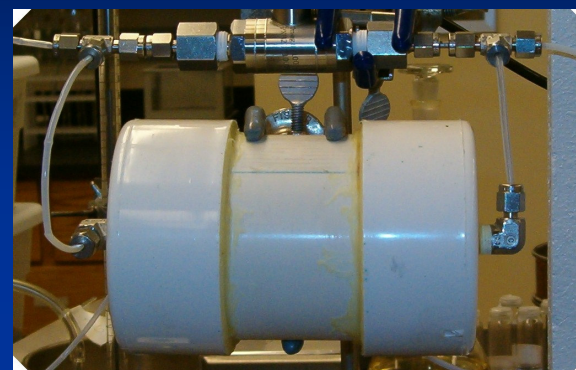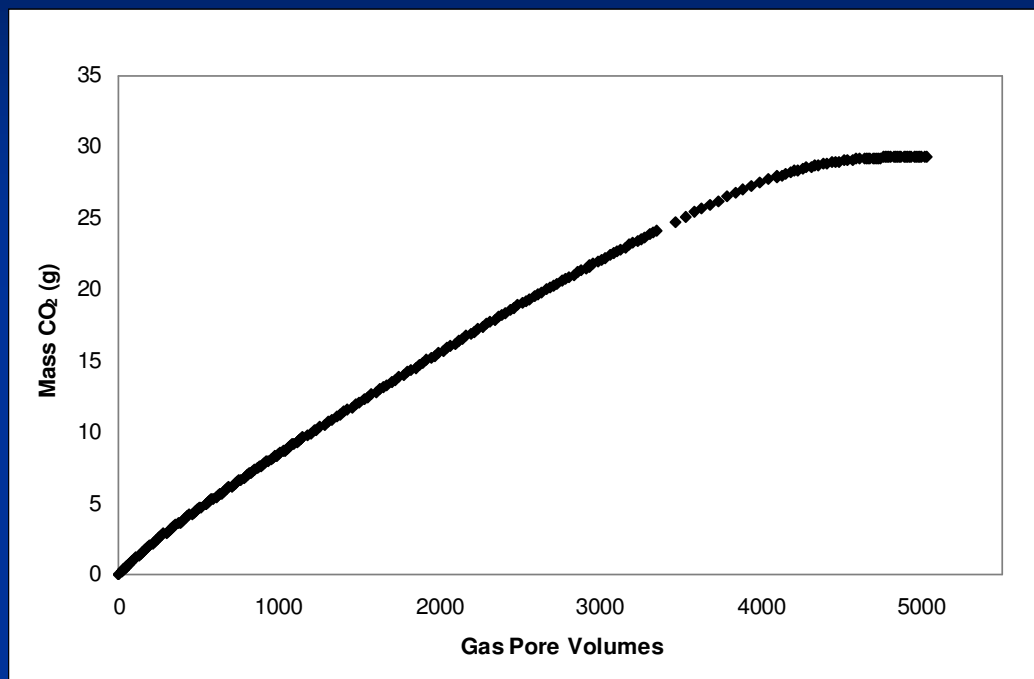
COLUMN:
13.6 cm long
7.3 cm diameter
Influent CO_2 conc. = 50,000 ppm_v
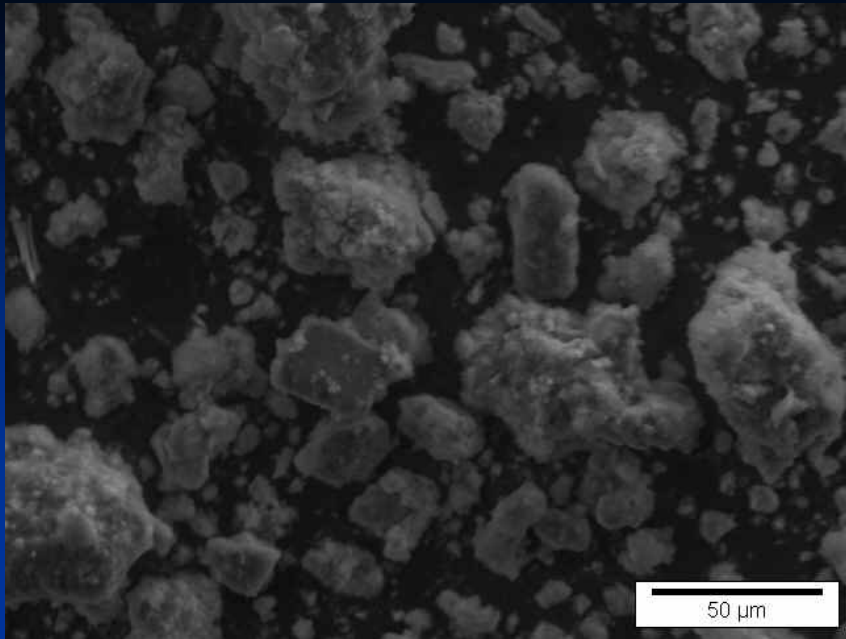Initial moisture content = 68%
Final moisture content = 55%
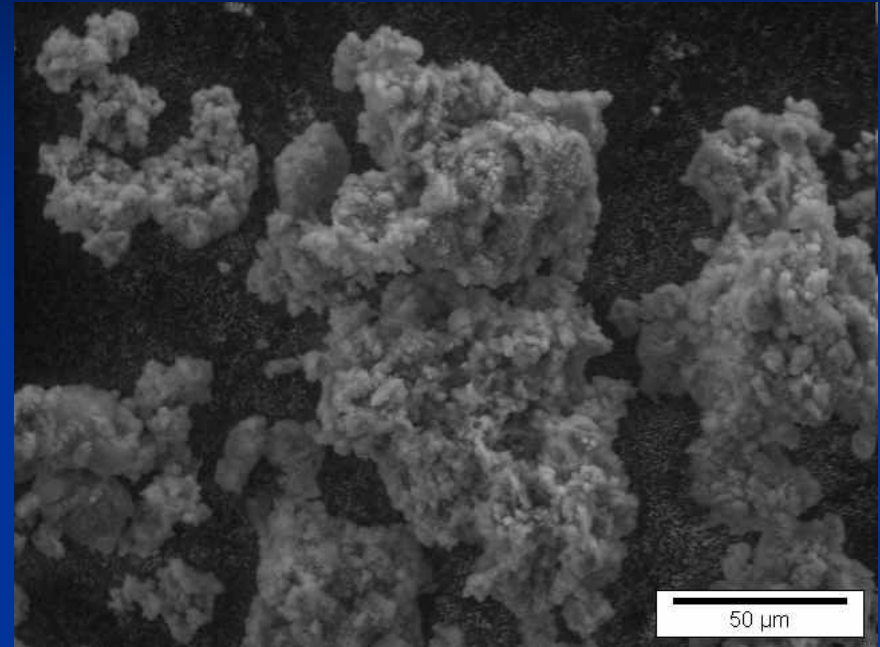Gas pore volume = 139 ml
Gas pore velocity = 5.5 cm/min

Assume CaO % =	30.00
Total mass CO2 seq =	28.48 g	*(accounts for CO2 removed in N2 flush)*
Mass CaO consumed =	36.24 g
% CaO Conversion =	**28.49**
	no humidity added

Change in mass of column = 28.86 g
(mass balance > 98%)
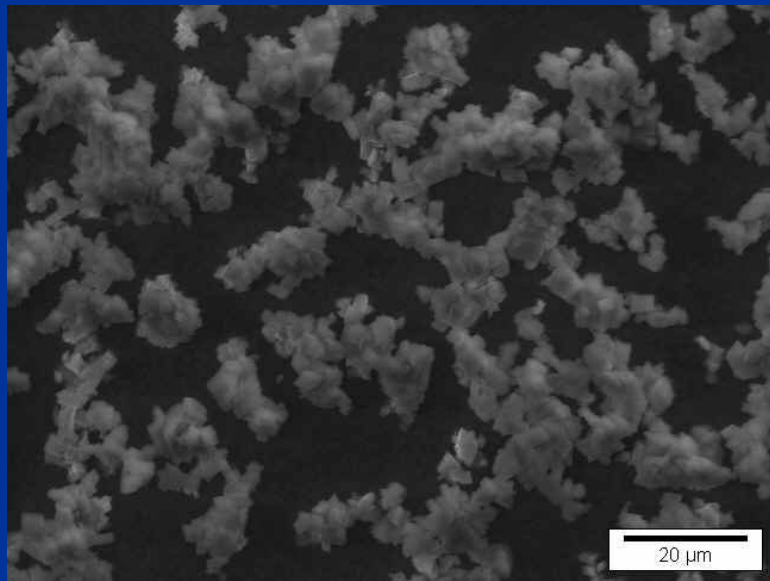
Duration of Experiment: 13 days

ESEM

Unreacted CKD, 500x

Pure grade CaCO$_3$, 100x

Reacted CKD from column experiment; Sample taken from inlet, center

CO$_2$ and H$_2$O vapor environment, 500x

Conclusions

- CaO, Ca(OH)$_2$, and CKD readily and rapidly sequester CO$_2$ under moist conditions

- The extent of sequestration is less than the "theoretical" amount either because coatings are formed or the influent gas flows preferentially

- The nature of the reactants and the specific products of the sequestration reactions are uncertain

- Environmental scanning electron microscopy shows promise for investigating the reactions and processes affecting sequestration rates and extent

Important Research Questions

- Carbonation reaction mechanism(s)
  - What are the rate-limiting processes?

- Rate of reaction(s)
  - Does the reaction rate change with time?
  - Does mechanism change with time?

- Extent of sequestration
  - What role does water and oxide composition play in reactions?

- Pattern of precipitation (pore filling, film or coating on particles, micropore filling, etc.)
  - Is pore plugging significant?
  - Does precipitation hinder/change gas transport?

- CO_2 gas transport
  - How important is preferential flow (immobile zones)?
  - How important is gas dispersion and diffusion?

Acknowledgements